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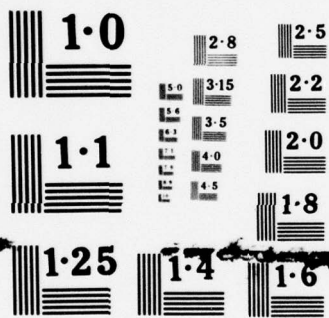   JUN 78 R ROE   N00014-77-C-0376
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Evaluation of the Polymer-Polymer Interaction Parameter

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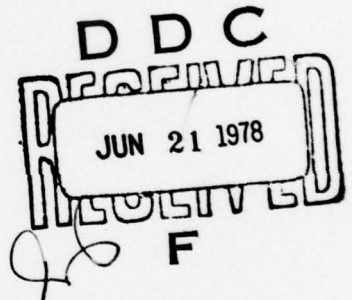
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The strength of interaction between the segments of dissimilar components greatly influence the morphology of micro-domains and hence the properties of polymer-polymer blends and block copolymers. In the theories of polymer-polymer interfaces

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dealing with such multicomponent systems, the interaction between components is usually expressed in terms of a single parameter which is independent of concentration. The validity of such an approximation is examined in this work in the light of the equation-of-state thermodynamic theory of polymer solutions and mixtures developed by Flory and coworkers. Using the molecular parameters evaluated by these workers, we have computed the free energy of mixing for the pairs, polyethylene/polyisobutylene, polyisobutylene/polystyrene and natural rubber/polystyrene. The results show that the polymer-polymer interaction parameter Λ, defined as the residual free energy of mixing divided by the product of volume fractions ϕ_1 ϕ_2, is only moderately dependent on concentration and temperature. This is in contrast to the trend expected of Λ for the polymer pairs which are compatible at normal temperatures because of special interactions between the components. The present results justify the use of a constant polymer-polymer interaction parameter in the interface theories for incompatible polymer systems.

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INTRODUCTION

The morphology and properties of polymer-polymer blends and block copolymers depend to a large measure on the strength of interaction between the two, chemically different components in the system. The degree of separation into distinct phases, the thickness of the interface between them and the size and shape of the block copolymer domains are some of the important features which are governed largely by the polymer-polymer interaction.

There are now available a number of theoretical treatments[1-8] dealing with the problem of polymer compatibility and the polymer-polymer interfaces either in polymer blends or in block copolymers. These theories differ from each other greatly in the way they evaluate the entropic effect of domain formation, i.e., the restrictions to the polymer chain conformations imposed by the presence of the interface. However, most of them share a common approximation in which the energetic interaction between two dissimilar polymer segments is represented by a single parameter, usually denoted by χ, which is assumed to be a function of temperature only for a given polymer-polymer pair. The χ parameter was originally introduced in the polymer solution thermodynamics to represent the van Laar heat of interaction. It was soon realized, both experimentally and theoretically, that the value of χ is not a constant for a given polymer-solvent pair, but depends on the concentration (and to some extent on the molecular weight) of the polymer, and also that a sizable contribution of an entropic

nature to χ has to be admitted in order to account for its temperature dependence.

When attempting to utilize these polymer interface theories[1-8] in planning and interpreting experiments, we encounter two problems associated with the interaction parameter in polymer-polymer systems. First we have to find a way of determining the values of the interaction parameters for the polymer pairs of interest. There is as yet no general experimental procedure which allows us evaluation of the χ parameter. Without reliable values of the χ parameter, comparative tests of the competing theories can only be made qualitatively. Secondly, in order to be able to utilize these theories with more confidence we have to have some idea about the dependence of the χ parameter on concentration, temperature, etc.

The equation-of-state thermodynamics, recently developed by Flory and his coworkers[9-11], has achieved a considerable improvement in treating the thermodynamics of polymer solutions over the classical Flory-Huggins type solution theory. Whereas in the latter the volume change on mixing is ignored, the newer theory takes account the equation-of-state contribution, or the contribution by the change in free volume on mixing, to the free energy of mixing. In this work we evaluate the polymer-polymer interaction parameters for a few polymer pairs of interest, by closely following the method of calculation suggested by the Flory equation-of-state thermodynamics and utilizing the values of molecular parameters of component polymers evaluated by them. The results are examined to gain insight into the

dependence of the interaction parameter on various physical parameters of the system such as the concentration and temperature.

EVALUATION OF THE POLYMER-POLYMER INTERACTION PARAMETER

The strength of polymer-polymer interaction is represented here by a new parameter Λ instead of the usual χ. The "polymer-polymer interaction parameter" Λ is defined by the following equation:

$$\Delta G_M = RT \left(\frac{1}{V_1} \phi_1 \ln \phi_1 + \frac{1}{V_2} \phi_2 \ln \phi_2 \right) + \Lambda \phi_1 \phi_2 \qquad (1)$$

where ΔG_M is the free energy of mixing per unit volume of the mixture, V_1 and V_2 are the molar volumes of the polymers 1 and 2, and ϕ_1 and ϕ_2 are the volume fractions of the two polymers in the mixture. The first term represents the usual combinatorial entropy of mixing and therefore the term containing Λ includes all other contributions to the free energy of mixing. Λ thus includes the enthalpic interaction between the two components but also the effect of entropy changes unaccounted for by the simple combinatorial term.

It has the dimension of energy per unit volume. When both Λ and χ are independent of concentration, Λ is equal to $\chi RT/V_2$. When χ varies with concentration the relation between Λ and χ is a little more complex because χ in polymer solution theories is usually defined in terms of the excess chemical potential rather than the excess free energy of mixing given in Equation (1). The polymer-polymer interaction parameters appearing in various theories of interfaces[1-8] are usually defined with

regard to the local free energy of mixing, and therefore the definition of Λ given in Equation (1) is more appropriate than the one given in terms of the excess chemical potential.

There are other advantages of the above definition of Λ, one of them being the fact that the values of χ depend on the assumed volume of a polymer segment (usually taken equal to the volume of the solvent molecule V_2), while Λ is defined per unit volume of the mixture. Another advantage is that the values of Λ can be related approximately to the solubility parameters of the components δ_1 and δ_2 by:

$$\Lambda = (\delta_1 - \delta_2)^2 \qquad (2)$$

In the Flory equation-of-state theory, the thermodynamic properties of a pure component liquid (either monomeric or polymeric) are represented completely by means of three characteristic constants, v_1^*, T_1^*, and p_1^*, which can be evaluated from the p-V-T and other thermodynamic properties of the liquid. The equation-of-state thermodynamics then recognizes three types of contributions to the free energy of mixing two liquid components. The first is the one due to the combinatorial entropy of mixing as expressed by the first term in Equation (1). The second is the change in enthalpy, ΔH_M, contact, arising from creation of 1, 2 nearest neighbor contacts on mixing. The third is the free volume (or the equation-of-state) contribution resulting from the change in volume on mixing. This latter contribution contains both enthalpic and entropic components, $\Delta H_{M,fv}$ and $-T\Delta S_{M,fv}$. The quantities, expressed per unit volume

of the mixture, are given by:

$$\Delta H_{M, \text{ contact}} = X_{12} \; \theta_2 \; \phi_1 / \tilde{v}^2 \tag{3}$$

$$\Delta H_{M, fv} = \sum_{i=1,2} \; \phi_i \; p_i^* \; (\tilde{v}_i^{-1} - \tilde{v}^{-1}) / \tilde{v} \tag{4}$$

$$-T\Delta S_{M, fv} = \sum_{i=1,2} 3\tilde{v}^{-1} \; \phi_i \; p_i^* \; \tilde{T}_i \; x \; \ln \; [(\tilde{v}_i^{\frac{1}{3}} - 1)/(\tilde{v}^{\frac{1}{3}} - 1)] \tag{5}$$

where $\tilde{v}_1 = v_1/v_1^*$, $\tilde{T}_1 = T_1/T_1^*$, and the unsubscripted quantities refer to the mixture.

To evaluate the expressions (3) - (5) one needs, in addition to the characteristic parameters v_i^*, p_i^*, T_i^* for each component, the value of X_{12} denoting the energy change on contact of 1, 2 polymer segments, and the surface fraction θ_2 defined by:

$$\theta_2 = \frac{\phi_2}{\phi_1 \; (s_1/s_2) + \phi_2} \tag{6}$$

where s_1/s_2 denotes the ratio of surface areas of the two types of segments (occupying equal volumes). The derivation of the expressions (3) to (5) and more precise meaning of the various symbols can be found in the original papers[9-11] by Flory and coworkers.

In view of (3) - (5), Λ defined in Equation (1) can be expressed as:

$$\Lambda = \Lambda_{h, \text{ contact}} + \Lambda_{h, fv} + \Lambda_{s, fv} \tag{7}$$

where

$$\Lambda_{h, \text{ contact}} = \Delta H_{M, \text{ contact}} / \phi_1 \; \phi_2 \tag{8}$$

$$\Lambda_{h,fv} = \Delta H_{M,fv} / \phi_1 \phi_2 \tag{9}$$

and

$$\Lambda_{s,fv} = -T\Delta S_{M,fv} / \phi_1 \phi_2 \tag{10}$$

RESULTS AND DISCUSSIONS

Three polymer pairs, polyethylene(PE)/polyisobutylene(PIB), PIB/polystyrene(PS) and natural rubber(NR)/PS, are considered. The characteristic parameters, v^*, p^*, T^* for each of these polymers have been evaluated by Flory and coworkers and are used here as given.

The first pair, PE/PIB, has already been examined by Flory, Eichinger and Orwoll[12] to ascertain their possible mutual compatibility. For this pair X_{12} and s_1/s_2 were given as 0.20 ± 0.10 cal/cc and $1/0.72$, respectively, the former determined as a result of their examination of a series of mixtures of PIB with n-alkanes.

For the PIB/PS pair, we take X_{12} equal to ca. 40 J/cm^3 (9.6 cal/cc), since four systems consisting of an aromatic and an aliphatic component were found to give similar values of X_{12}: 42 J/cm^3 for PIB/benzene[13], 42 J/cm^3 for cyclohexane/benzene[14], 40 J/cm^3 for n-heptane/benzene[14] and 42 J/cm^3 for cyclohexane/ PS[15]. The ratio s_1/s_2 can be determined by examination of the molecular models of respective polymer segments. In order to avoid introducing any additional parameters which could be construed as adjustable, we obtained the s_1/s_2 ratio of 1.24 for PIB/PS by multiplying the s_1/s_2 ratios 0.62 for PIB/cyclohexane[16]

and 2.0 for cyclohexane/PS[15] which were determined in the previous studies of these polymer-solvent systems.

The value of X_{12} for benzene/natural rubber was given[10] as 1.40 cal/cc. In the absence of any other data on similar systems, we have taken X_{12} for NR/PS to be also 1.40 cal/cc, on the assumption that the interaction of NR segments with any aromatic component is likely to be similar. The value of s_1/s_2 for NR/PS is taken as 1.9 equaling the product of the previously reported values of the ratio: 0.90 for NR/benzene[10], 1/0.58 for benzene/PIB[13] and 1.24 for PIB/PS.

The values of the polymer-polymer interaction parameter Λ, calculated by use of the X_{12} and s_1/s_2 values discussed above for the three polymers pairs, are tabulated in Table I. In order to show the concentration dependence, these values are given for each pair at three different concentrations, corresponding to the weight fraction w_1 of the first component equal to 0.1, 0.5, and 0.9.

For PE/PIB, both aliphatic hydrocarbons, the exchange energy parameter X_{12} is very small, and the largest contribution to Λ arises from the free volume entropy effect. The reduced volume $\tilde{v} = v/v^*$ changes from 1.182 for PE and 1.149 for PIB to the intermediate value of 1.166 for the mixture at $w_1 = 0.5$. The net excess volume of mixing predicted is very small (and positive). However, the changes in enthalpy and entropy of each component arising from their respective changes in the free volume on mixing (i.e. the individual terms in expressions (4) and (5)) fail to cancel each other completely, and the net

difference, especially the entropy effect represented by $\Lambda_{s,fv}$, remains positive and finite. It magnitude, although fairly small in absolute terms, is still larger than the contact enthalpy term $\Lambda_{h, contact}$. Even if X_{12} were zero, the PE/PIB pair would have been incompatible because of the free volume effect.

For PIB/PS, the large X_{12} value gives rise to a repulsion and a consequent small expansion of free volume on mixing. The $\tilde{v}$ values for the two components are fairly similar ($\tilde{v}$ = 1.149 and 1.153 for PIB and PS, respectively). Although the $\tilde{v}$ value of 1.154 for the mixture at w_1 = 0.5 indicates expansion of the free volume on mixing, the resulting changes in enthalpy and entropy, as represented by $\Lambda_{h,fv}$ and $\Lambda_{s,fv}$, happen to cancel each other almost completely. The Λ value for PIB/PS therefore arises solely from the contact term $\Lambda_{h, contact}$.

The NR/PS pair is of more interest here because of its similarity to polybutadiene/PS and polyisoprene/PS which are the pairs most widely studied in block copolymer systems. No excess volume of mixing is predicted for this pair, the $\tilde{v}$ values, 1.172 for NR and 1.152 for PS, changing to 1.162 for the mixture at w_1 = 0.5. Although $\Lambda_{h,fv}$ and $\Lambda_{s,fv}$ fail to cancel each other completely, the net sum of the two is still only about 10% of the total Λ, indicating that here too the contact term is the most important effect giving rise to the incompatibility of the pair.

In describing the polymer-polymer interaction parameters for pairs which are normally incompatible as those discussed in

this work, it therefore appears that the free volume (or the equation-of-state) contribution can usually be neglected except when the pair is on the verge of compatibility. This is in a marked contrast to polymer-solvent systems where the free volume effect is usually very large. From this follows that the dependence of Λ for polymer-polymer pairs on concentration or on temperature would also be fairly small. Table I shows only a modest variation of Λ with a change in w_1 from 0.1 to 0.9. The relatively more pronounced variation of Λ for NR/PS as compared to other two pairs still arises mostly from the contact enthalpy term and reflects the larger s_1/s_2 ratio for this system.

The temperature dependence of Λ is summarized in Table II. It shows that Λ can be taken for practical purposes as being independent of temperature. No similar calculation was made for NR/PS because the characteristic parameters for NR at temperatures other than 25°C are not available. It is however very likely that Λ for NR/PS would also be fairly independent of temperature, in view of the dominant contribution to Λ by the contact enthalpy term as discussed above.

The fact that Λ is positive and fairly independent of temperature for these three pairs of polymers means that as the temperature is raised, their degree of incompatibility will diminish and the interfacial boundary between phases will become more diffuse. In the case of block copolymer systems the constraint imposed by the requirement that the block joints be at the domain boundaries provides additional free energy term

to make the mixing more favorable. Thus, when the block lengths are fairly moderate, the first term in Equation (1) will become sufficiently large and negative to render the two blocks thermodynamically miscible. Evidence of such homogenization of a styrene-butadiene-styrene block copolymers at increased temperature has been reported from rheological studies[17,18].

There are currently known[19] several polymer pairs, such as PS/poly(vinyl methyl ether)[20,21], which appear to be truly compatible thermodynamically. In most of these the compatibility probably arises from specific interactions other than dispersion forces which make Λ for the pair negative. The increase in temperature will generally weaken the specific interaction and the increasingly unfavorable free volume effect[22] will eventually make Λ positive. Thus these compatible pairs will in general exhibit a lower critical solution temperature phenomenon on heating. In contrast, the three polymer pairs discussed in this work are, at room temperature, all below their upper critical solution temperature. The thermodynamic properties of block copolymers formed from these polymer pairs can therefore be discussed in terms of a constant polymer-polymer interaction parameter Λ without referring to the possible complications arising from the free volume effect. In this vein it seems unlikely that a styrene/α-methylstyrene block copolymer[23] will exhibit enhanced domain segregation on raising the temperature.

It is gratifying to see that the value of Λ for NR/PS given in Table I is in excellent agreement with 0.8 cal/cc

which was estimated by Meier[3b] for polybutadiene/PS from the solubility parameter difference. It is, however, doubtful that the present approach of utilizing the equation-of-state data can ever be a practical means of evaluating Λ. A reliable value of X_{12} for a polymer-polymer pair can be estimated only when data on a number of similar polymer-solvent systems are available. There is also a theoretical difficulty arising from the unsymmetric definition of X_{12}, so that $X_{21} \neq X_{12}$. In the treatment of polymer-solvent systems, an additional entropic term containing a parameter Q_{12} was often introduced to achieve good agreement between theory and experiment, but it is difficult to estimate the error arising from omission of this term for polymer-polymer systems.

Because of these uncertainties, equations (1) - (5) may not be relied upon as a means of quantitative evaluation of Λ until more data for other polymer-solvent systems become available. The equation-of-state thermodynamics is, however, useful in its ability to give us insight into the physical factors and their relative magnitudes which contribute to the polymer-polymer interaction parameter. The results in this work clearly show that the dependence of Λ on concentration and temperature is moderate. This gives a justification as a good approximation to the use of a constant polymer-polymer interaction parameter in the polymer interface theories where the polymer concentration encompases the whole range $w_1 = 0$ to 1 across the phase boundary.

ACKNOWLEDGMENT

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TABLE I

POLYMER-POLYMER INTERACTION PARAMETER Λ AND ITS COMPONENTS

	w_1	Λ	$\Lambda_{h,\,contact}$	$\Lambda_{h,fv}$	$\Lambda_{s,fv}$
PE/PIB at 25°C	0.1	0.33	0.14	-0.03	0.22
	0.5	0.30	0.12	-0.03	0.21
	0.9	0.27	0.11	-0.03	0.20
PIB/PS at 25°C	0.1	7.02	7.02	1.20	-1.20
	0.5	6.49	6.48	1.10	-1.09
	0.9	5.96	5.95	1.00	-0.99
NR/PS at 25°C	0.1	1.03	0.95	0.14	-0.06
	0.5	0.78	0.70	0.11	-0.03
	0.9	0.64	0.56	0.09	-0.01

Note: Λ in cal/cc

TABLE II

TEMPERATURE DEPENDENCE OF Λ

	Temp.(°C)	Λ	$\Lambda_{h, contact}$	$\Lambda_{s,fv}$	$\Lambda_{h,fv}$
PE/PIB at w_1 = 0.5	25	0.30	0.12	-0.03	0.21
	100	0.28	0.11	-0.04	0.20
	150	0.26	0.11	-0.04	0.19
PIB/PS at w_1 = 0.5	0	6.53	6.52	1.02	-1.01
	25	6.39	6.38	1.10	-1.08
	100	6.00	5.99	1.31	-1.30